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Background Hydrocarbon Residues in Fishes from the Great Lakes and Eastern Montana

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16. ABSTRACT

For the past eight years, this laboratory has been conducting GC/MS exploration studies of organic chemical residues in fishes from major U.S. watersheds. One of the frequently occuring classes of chemicals isolated by multi-class analytical techniques, such as gel permeation chromatography, is n-alkanes. Odd-numbered alkanes with 13-19 carbon atoms are often the most abundant, and are predominanted by n-heptadecane. The presence of these compounds seem to indicate normal biosynthesis in aquatic ecosystems (MCINNES et al. 1980), whereas their absence or the presence of other hydrocarbon mixtures which obscure the natural hydrocarbons may be indicative of an adverse impact on the ecosystem (VEITH et al. 1979).

This study presents quantitative data for background levels of these compounds in fishes from selected eastern Montana watersheds. Sampling sites were chosen to represent watersheds having coal extraction and conversion activities and those that do not. In comparison, data is also presented for Great Lakes fish.

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Background Hydrocarbon Residues in Fishes from the Great Lakes and Eastern Montana

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For the past eight years, this laboratory has been conducting GC/MS exploration studies of organic chemical residues in fishes from major U.S. watersheds. One of the frequently occuring classes of chemicals isolated by multi-class analytical techniques, such as gel permeation chromatography, is n-alkanes. Odd-numbered alkanes with 13-19 carbon atoms are often the most abundant, and are predominanted by n-heptadecane. The presence of these compounds seem to indicate normal biosynthesis in aquatic ecosystems (MCINNES et al. 1980), whereas their absence or the presence of other hydrocarbon mixtures which obscure the natural hydrocarbons may be indicative of an adverse impact on the ecosystem (VEITH et al. 1979).

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EXPERIMENTAL PROCEDURES

Sample Preparation. Fish samples from the Great Lakes were collected by state and federal field crews and shipped frozen to the Environmental Research Laboratory, Duluth, MN. Fish samples from southeastern Montana watersheds were collected by associates at Eastern Montana College, Billings, MT, and shipped in the same manner.

After receipt in the laboratory, fish samples were homogenized and frozen at -15°C. Subsamples of 20 g were Soxhlet-extracted with a 1:1 mixture of hexane/dichloromethane. The solvent was removed with a Kuderna-Danish (K-D) apparatus and the resulting oil was diluted to 100 mg/mL. The samples were then cleaned-up by gel permeation chromatography (GPC) as previously described (KUEHL & LEONARD 1978). The oil-free neutral fraction was concentrated in a K-D apparatus (ca. 1 mL) then passed through a 4 x 60 mm Celite 545 column saturated with 100% H_2SO_4. The eluent was concentrated (ca. 200 µL) and screened for adequate cleanup by GC prior to GC/MS analysis.

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Reagents and Standards. Hexane, dichloromethane, and cyclohexane (GPC) were distilled-in-glass quality (Burdick-Jackson). Hydrocarbon standards and 4,4'-dibromobiphenyl were obtained from Chem-Service, Inc.

GC/MS Analysis. Quantification of the n-hydrocarbons was done by multiple ion detection (MID) GC/MS using a Finnigan 4023 GC/MS/COM system. The GC was equipped with a 30 m x 0.25 mm SE-30 glass capillary column which was temperature programmed from 80 to 250°C at 4°/min. Solutions each containing n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, n-octadecane and n-nonadecane were prepared as external standards. 4,4'-Dibromobiphenyl was used as an internal standard for quantification by standard INCOS software. Fish sample solutions were concentrated or diluted as required to keep GC/MS peaks area within the range of standards.

Periodically throughout the analyses different concentrations of the external standards were analyzed (5 trials each). The overall accuracy (± 11.3% R.E.) and precision (± 11.1% R.E.) were calculated as the combined deviations from actual and average values, respectively, for the hydrocarbon standards. Full mass range (m/z 50-500) scanning GC/MS was used to verify the idenfification of the peaks quantified.

RESULTS AND DISCUSSION

Although hydrocarbon patterns are not often detected in routine pesticide monitoring using electron capture (EC) detectors, the predominance of these residues is readily apparent when flame ionization detectors (FID) or GC/MS systems are used. A typical FID chromatogram of the extract of lake trout from Lake Michigan is presented in Figure 1. The largest component in this extract is the n-heptadecane, although other n-paraffins are apparent. A summary of n-heptadecane concentrations in Great Lakes lake trout is presented in Table 1. These data are intended only to show typical concentrations in fish from several major watersheds.

TABLE 1. Concentrations of n-Heptadecane in Great Lakes Fish

Lake	Species	Concentration (µg/g - wet)	Concentration (µg/g - lipid)
Superior	Lake trout	7.1	21
Mighigan	Lake trout	6.6	170
Huron	Lake trout	47	230
Ontario	Lake trout	41	240

Results of the analyses of n-hydrocarbons in Montana fish samples as well as sample collection locations are presented in Table 2. The data show that the total n-hydrocarbon residue in the Montana fishes ranged from 1.3 µg/g to 160 µg/g. In the majority of the samples the odd-numbered n-hydrocarbons accounted for over 80% of the hydrocarbon residue. In 16 of the samples n-heptadecane was the predominant hydrocarbon; in two of the samples n-pentadecane levels were greater than that of n-heptadecane.

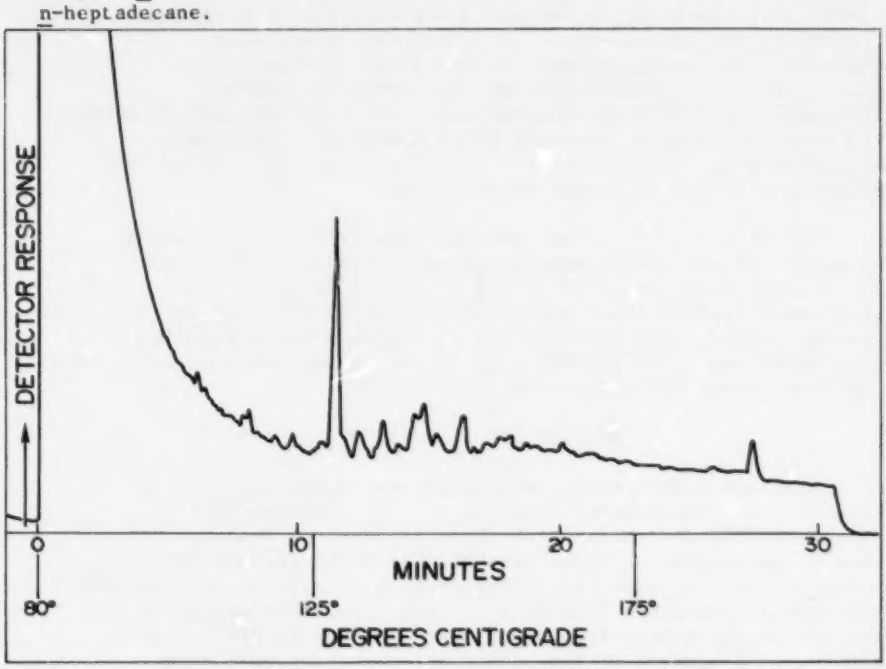

Fig. 1. Flame ionization gas chromatographic trace of a Lake Superior trout extract. The large peak between 10 and 12 min is n-heptadecane.

A hydrocarbon of molecular weight 288 (confirmed by methane chemical ionization mass spectrometry) was observed in some of the samples and was tentatively assigned the molecular formula of $C_{21}H_{36}$. The mass spectrum of this chemical lacked the 217 and 149 m/z ions characteristic of stearanes, the 191 m/z ions characteristic of triterpenes, or the 113 and 183 m/z ions characteristic of acyclic isoprenoids. A possible identity is henicosatetraene which has a molecular weight of 288 and has been found in both marine algae (YOUNGBLOOD et al. 1971; BLUMER et al. 1970) and in moss (KARUNEN 1974). These investigators found henicosatetraene and other methylene-interrupted polyolefins; however, our investigation gave no indication of the presence of these polyolefins residues in these freshwater fish.

TABLE 2

Hydrocarbon Residues in Fish from Eastern Montana Rivers

Sampling Area	Species[a]	Concentration of n-Hydrocarbons (ug/g-wet weight)						
		Tetradecane	Pentadecane	Hexadecane	Heptadecane	Octadecane	Nonadecane	Total
1. Tongue River Reservoir	White Sucker[b]	<0.1	0.1	0.1	2.8	0.1	0.4	3.4
2. Tongue River - Birney	FHM[c]	0.6	4.7	0.9	9.2	0.1	0.2	15.7
3. Tongue River - Miles City	FHM	<0.1	3.6	0.2	5.8	0.2	1.5	11.3
4. Otter Creek - Ashland	FHM	<0.1	0.4	0.1	2.4	0.1	0.4	3.4
5. Pumpkin Creek - Miles City	FHM	0.5	42.5	7.4	11.1	2.7	8.5	72.2
6. Little Powder River - Broadus	White Sucker	0.1	3.5	1.3	39.4	3.4	23.0	70.6
7. Powder River - Locate	Flathead Chub[d]	<0.1	0.3	0.2	6.6	2.1	2.9	12.1
8. Powder River Mouth	Flathead Chub	<0.1	0.6	0.3	15.2	2.6	3.7	22.4
9. Box Elder Creek - Ekalaka	FHM	0.1	4.7	0.4	5.0	0.2	1.2	11.6
10. O'Fallon Creek - Mill Iron	White Sucker	<0.1	0.1	0.1	0.6	0.1	0.4	1.3
11. Beaver Creek - Baker	White Sucker	<0.1	97.6	2.5	55.9	<0.1	2.1	158
12. Sunday Creek - Miles City	FHM	<0.1	0.2	0.6	2.8	<0.1	0.2	3.8
13. Big Porcupine Creek - Forsyth	FHM	<0.1	0.5	0.1	3.8	0.2	0.5	5.1
14. Sarpy Creek - Sanders	FHM	<0.1	1.0	0.1	3.5	0.2	0.6	5.4
15. Big Horn River - Hardin	Lake Chub[e]	<0.1	0.8	0.4	15.3	0.7	5.0	26.2
16. Unnamed Creek - Hardin	FHM	<0.1	0.4	0.1	2.8	0.1	0.3	3.7
17. Musselshell River - Melstrum	Silvery Minnow[f]	0.1	5.4	0.4	2.2	0.2	0.2	8.5
18. Hanging Women Creek - Birney	White Sucker	<0.1	0.6	0.2	3.8	0.1	0.5	5.2

[a] Composite samples of 2-10 fish.

[b] Catostomus commersoni

[c] Fathead minnow, Pimephales promelas

[d] Hybopsis gracilis

[e] Couesius plumbeus

[f] Hybiognathus nuchalis

In addition to the n-paraffins reported in Table 2, smaller quantities of corresponding unsaturated hydrocarbons were identified. These included pentadecene, heptadecene, heptadecadiene, octadecene, nonadecene, nonadecadiene, and dodecadiene. More than one isomer for the unsaturated hydrocarbons was observed on the capillary column. Although structures were not unequivocally determined, they are likely to parallel those found in the marine environment which have double bonds in the 3 or higher positions (YOUNGBLOOD et al. 1971; BLUMER et al. 1971). No evidence for cycloalkyl hydrocarbons was found.

All of the Montana samples were collected in watersheds which are predominately used for grazing. There was no apparent relationship between the hydrocarbon residues and discernible land-uses and/or industrial discharges which would lead to hydrocarbon pollution of the watershed. The absence of other hydrocarbon residues which would indicate petroleum products such as lubricating or fuel oils, and the pattern of odd-number hydrocarbons with no comparable even-number hydrocarbons suggest that these residues are biogenic in origin. We propose that the composition and quantities of these residues may be used to establish baseline residues for hydrocarbons in natural waters.

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